TABLE V

RESULTS OF CORRELATIONS OF η_X WITH EQ 4

Set	α	β	h	R^a	F^b	r^c	$s_{estd}{}^d$	$s_\alpha{}^d$	$s_\beta{}^d$	s_h	n^e	CL[f]
I	0.767	0.521	−0.00709	0.998	206.0	0.181	0.0227	0.0443	0.0717	0.0216	5	99.5
II	0.668	0.529	−0.0635	0.861	11.48	0.0216	0.131	0.183	0.175	0.0789	11	99.5
IIA	0.666	0.622	−0.0272	0.913	17.64	0.0299	0.111	0.155	0.155	0.0690	10	99.5
IIB	0.620	0.788	−0.0324	0.956	31.50	0.0929	0.0866	0.122	0.141	0.0598	9	99.9

[a] Multiple correlation coefficient. [b] F test for significance of regression. [c] Partial correlation coefficient of σ_I on σ_R. [d] Standard error of the estimate, α, β, and h. [e] Number of points in set. [f] Confidence level.

are presented in Table V. Excellent correlations were obtained. Some improvement in the correlation of η_X (1,4-benzoquinone) resulted from the exclusion of η_{CO_2Me} from the (set IIA). The results were further improved by the exclusion of η_{Ac} (set IIB).

The magnitude and composition of the electrical effects on π-acceptor strength are comparable with those observed previously[1] for π-donor strength. The correlations with eq 4 permit the calculation of η values for a wide range of acceptors.

A Comparison of Peroxide and Ether Groups as Proton Acceptors in Intramolecular Hydrogen Bonding of Alcohols

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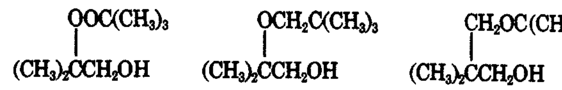
The differences in frequencies between the free and intramolecularly hydrogen-bonded O–H absorption ($\Delta\nu$) are presented along with the enthalpies of intramolecular hydrogen bonding ($-\Delta H_{IB}$) for 2-*t*-butylperoxy-2-methyl-1-propanol (I), 2-methyl-2-neopentoxy-1-propanol (II), and 3-*t*-butoxy-2,2-dimethyl-1-propanol (III) in carbon tetrachloride solution. By comparison with the model ethers (II and III), it is suggested that the hydroxy peroxide I exhibits intramolecular hydrogen bonding *via* a 1,5 interaction. Further comparison of $\Delta\nu$ and $-\Delta H_{IB}$ values for the hydroxy ether (II) and the hydroxy peroxide (I) indicates that the peroxide group is somewhat less basic than the ether group. With reference to suitable model compounds, the effect of *gem*-dimethyl substitution is discussed in light of the Thorpe–Ingold effect.

In the course of a long-range program designed to study the intramolecular reactions of substituted peroxides[1] we were led to investigate intramolecular hydrogen bonding to a peroxide group. A recent review[2] has compiled infrared intramolecular hydrogen bonding data for over 1600 compounds with the hydroxyl group as the proton donor. A number of compounds were listed having an ether oxygen as the proton acceptor. As yet no intramolecular hydrogen-bonding data has been reported for compounds with a peroxide linkage as the proton acceptor. A comparison is now made between peroxide and ether groups as proton acceptors in intramolecular hydrogen bonding where the hydroxyl group is the proton donor. The comparison is made between three stereochemically similar compounds: 2-*t*-butylperoxy-2-methyl-1-propanol (I), 2-methyl-2-neopentoxy-1-propanol (II), and 3-*t*-butoxy-2,2-dimethyl-1-propanol (III). Either 1,5 or 1,6 intramolecular hydrogen bonding is possible in I, while hydrogen bonding is restricted to a 1,5 interaction in II and a 1,6 interaction in III.

Results

In a preliminary communication, which was directed to another phase of our work, the synthetic routes to alcohols I and II were outlined.[3] The alcohols were oxidized to the corresponding acids with chromic acid, and evidence was presented for the structures of the acids.[3] Further evidence for the structures of I and II as well as III is presented in the Experimental Section.



I II III

At the concentrations which the spectra were measured only a free and a single hydrogen-bonded oxygen–hydrogen absorption was noted for the three alcohols (I, II, and III). No significant change was observed in the ratios of absorptivity over the concentration range 4.00×10^{-2}–10^{-3} M for the three alcohols. This ensures that the absorption due to hydrogen bonding represents only intramolecular hydrogen bonding.

The enthalpy of intramolecular hydrogen bonding was determined from a study of the effect of temperature on the ratio of the integrated absorbancies for the hydrogen bonded to free species (A_B/A_F). The data for the three alcohols are presented in Tables I–III.

TABLE I

INTEGRATED ABSORBANCIES FOR 2-*t*-BUTYLPEROXY-2-METHYL-1-PROPANOL (I) IN CARBON TETRACHLORIDE SOLUTION[a]

Temp, °C	A_F	A_B	A_B/A_F
33.8	55.0 ± 0.2	765.3 ± 2.6	13.9
49.9	57.8 ± 0.5	752.0 ± 1.8	13.0
70.1	60.5 ± 0.5	712.5 ± 1.5	11.8

[a] 4.00×10^{-2} M.

(1) Part I: W. H. Richardson, J. W. Peters, and W. P. Konopka, *Tetrahedron Lett.*, 5531 (1966).

(2) M. Tichý, *Advan. Org. Chem.*, **5**, 115 (1965).

(3) W. H. Richardson and R. S. Smith, *J. Amer. Chem. Soc.*, **89**, 2230 (1967).

TABLE II
INTEGRATED ABSORBANCIES FOR 2-METHYL-2-NEOPENTOXY-1-PROPANOL (II) IN CARBON TETRACHLORIDE SOLUTION[a]

Temp, °C	A_F	A_B	A_B/A_F
34.6	52.7 ± 0.4	366.7 ± 1.1	6.96
50.2	58.5 ± 0.5	376.5 ± 1.6	6.44
69.9	58.9 ± 0.5	342.1 ± 1.1	5.81

[a] 4.00 × 10^{-2} *M*.

TABLE III
INTEGRATED ABSORBANCIES FOR 3-*t*-BUTOXY-2,2-DIMETHYL-1-PROPANOL (III) IN CARBON TETRACHLORIDE SOLUTION[a]

Temp, °C	A_F	A_B	A_B/A_F
33.8	148.0 ± 0.4	1145.5 ± 3.3	7.74
50.0	151.2 ± 1.2	1054.0 ± 4.8	6.97
69.9	161.6 ± 1.1	981.0 ± 4.2	6.07

[a] 4.00 × 10^{-2} *M*.

Each value of A_F and A_B is an average of ten integrations by a planimeter. Values of the enthalpy of intramolecular hydrogen bonding were calculated according to eq 1[4] by using a least-squares computer program.

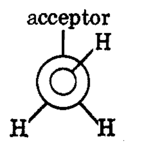
$$\frac{\partial(\log A_B/A_F)}{\partial(1/T)} = -\frac{\Delta H_{IB}}{2.303R} \quad (1)$$

The method of calculation assumes that the ratio of molar extinction coefficients (ϵ_B/ϵ_F) is temperature independent.[5] Typical of intramolecular hydrogen-bonding studies, only the enthalpy may be calculated. To calculate the free energy and thus entropy, the values of ϵ_F and ϵ_B are required.[5]

The differences in frequencies ($\Delta\nu$) between the free (ν_F) and hydrogen-bonded (ν_B) absorptions have been used to evaluate the strength of the hydrogen bond.[2] These data for alcohols I, II, and III are presented in Table IV along with the corresponding enthalpies.

Discussion

The $\Delta\nu$ values should represent the differences in frequencies between free O–H and hydrogen-bonded O–H stretching, without conformational changes of the O–H group.[2] The free O–H stretching frequency should be then associated with the conformation where the O–H bond is *gauche* between the hydrogen atom and the group containing the proton acceptor which is disposed on the carbon atom adjacent to the hydroxyl group (I_F, II_F, and III_F). The value of the free O–H



I_F, acceptor = $(CH_3)_2COOC(CH_3)_3$
II_F, acceptor = $(CH_3)_2COCH_2C(CH_3)_3$
III_F, acceptor = $(CH_3)_2CCH_2OC(CH_3)_3$

stretching frequency in various conformations is not easily resolved. The values of the free O–H stretching frequency may or may not be dependent on conformation. For example,[6] upon changing from a conformation where the hydroxyl hydrogen atom is *gauche* between a hydrogen atom and either a methyl or cyano group, the frequency is lowered by about 13 cm^{-1}. In monosubstituted alcohols a frequency of 3640 cm^{-1} is assigned to the conformation where the hydroxyl hydrogen atom is *gauche* between two adjacent hydrogen atoms.[6b,c] In contrast, it is reported[7] that neopentyl alcohol has only a single sharp absorption at 3640 cm^{-1} despite the availability of two different kinds of conformations. Only a single free O–H absorption is observed for the three alcohols I, II, and III. We are left with two possible explanations for the single free O–H absorption. Either the conformation where the hydroxyl hydrogen atom is *anti* to the acceptor group is preferentially populated to the exclusion of conformers I_F, II_F, and III_F (the free O–H stretching frequency occurs at 3638 cm^{-1}) or both the *anti* and *gauche* conformers yield the same absorption frequency. Although we prefer the latter explanation, this difficulty will not alter our conclusions. Since the three alcohols show free O–H absorptions at the same frequency, it is clear that the acceptor group does not alter this absorption by polar effects.

Intramolecular hydrogen bonding in the hydroxy peroxide I is possible from either a 1,5 or a 1,6 interaction. Previous reports[8] suggest that the enthalpy of intramolecular hydrogen bonding is more favorable for the 1,6 than the 1,5 interaction. The $\Delta\nu$ values for both diols and hydroxy ethers are larger for a 1,6 than a 1,5 interaction. This conclusion makes the tacit assumption that enthalpy is simply related to $\Delta\nu$. Unfortunately, the Badger–Bauer rule,[9] which states that there should be a linear relationship between $-\Delta H$ and $\Delta\nu$ for *inter*molecular hydrogen bonding, has not met with success for intramolecular hydrogen bonding.[2,10] Considerable doubt may exist as to the differences in the enthalpy of intramolecular hydrogen bonding in series of compounds as reflected by $\Delta\nu$ values. Still another problem must be considered, namely, the entropy of intramolecular hydrogen bonding. Both the enthalpy and entropy must be known to evaluate whether 1,5 or 1,6 hydrogen bonding is more favorable. Unfortunately, only the enthalpy of intramolecular hydrogen bonding can be measured. This results from the fact that the molar extinction coefficients for the free and hydrogen bonded absorptions are not necessarily the same and may also vary from one compound to another.

It is clear from our data that the enthalpy of intramolecular hydrogen bonding is more favorable for the 1,6 than the 1,5 interaction by comparing the ΔH_{IB} values for II and III. The difference in entropy of intramolecular hydrogen bonding ($\Delta\Delta S_{IB}$) between the five- and six-membered ring species may be estimated. The rotation of one additional bond is restricted in the six-membered ring species as compared with the five-

(4) See A. W. Baker and A. T. Shulgin, *Spectrochim. Acta*, **19**, 1611 (1963).
(5) W. H. Richardson and R. F. Steed, *J. Org. Chem.*, **32**, 771 (1967).
(6) (a) N. Mori, S. Ōmura, H. Yamakawa, and Y. Tsuzuki, *Bull. Chem. Soc.* (Tokyo), **38**, 1627 (1965); (b) M. Oki and H. Iwamura, *ibid.*, **32**, 950 (1959); (c) F. Dalton, G. D. Meakins, J. H. Robinson, and W. Zaharia, *J. Chem. Soc.*, 1566 (1962).
(7) L. Joris, P. von R. Schleyer, and E. Osawa, *Tetrahedron*, in press. We thank the authors for providing this information prior to publication.
(8) (a) N. Mori, S. Ōmura, and Y. Tsuzuki, *Bull. Chem. Soc.* (Tokyo), **38**, 1631 (1965); (b) L. P. Kuhn, *J. Amer. Chem. Soc.*, **74**, 2492 (1952); (c) A. B. Foster, A. H. Haines, and M. Stacey, *Tetrahedron*, **16**, 177 (1961).
(9) (a) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937); (b) R. M. Badger, *ibid.*, **8**, 288 (1940).
(10) The applicability of the Badger–Bauer rule to intermolecular hydrogen bonding has been a subject of debate. See (a) K. F. Purcell and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 2874 (1967); (b) R. West, D. L. Powell, L. S. Whately, M. K. T. Lee, and P. von R. Schleyer, *ibid.*, **84**, 3221 (1962); (c) D. L. Powell and R. West, *Spectrochim. Acta*, **20**, 983 (1964).

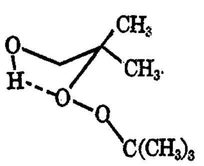
TABLE IV

VALUES OF $\Delta\nu$ and ENTHALPIES of INTRAMOLECULAR HYDROGEN BONDING FOR ALCOHOLS I, II, AND III

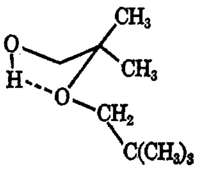
Alcohol	ν_F, cm^{-1}	ν_B, cm^{-1}	$\Delta\nu$, cm^{-1}	ΔH_{IB}, kcal/mol[a]
2-*t*-Butylperoxy-2-methyl-1-propanol (I)	3638	3593	45	-0.95 ± 0.05
2-Methyl-2-neopentoxy-1-propanol (II)	3638	3584	54	-1.07 ± 0.03
3-*t*-Butoxy-2,2-dimethyl-1-propanol (III)	3638	3510	128	-1.41 ± 0.05

[a] With probable error.

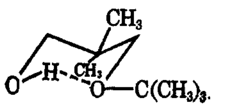
membered ring species. Empirical correlations suggest that the entropy should be lowered by 4.0 eu per restricted rotation.[11] At 50°, approximately the average temperature of the measurements, $T\Delta\Delta S_{IB}$ is about -1.3 kcal ($= 323(-4.0) \times 10^{-3}$). The difference in enthalpy between the 1,5 and 1,6 interaction as given by II and III is $\Delta\Delta H_{IB} = -0.34$ kcal ($= -1.41 - (-1.07)$). The free-energy difference between these two species is then equal to approximately $+1.0$ kcal ($\Delta\Delta G_{IB} = -0.34 - (-1.3)$). In other words, the 1,5 interaction is favored over the 1,6 interaction by about 1.0 kcal. This would suggest that the 1,5 interaction is also favored over the 1,6 interaction in the peroxy alcohol I. The intramolecular hydrogen bonded species may then be represented by the structures I_B, II_B, and III_B.



I_B



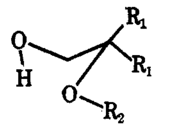
II_B



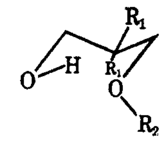
III_B

Several correlations have been made between the basicity of the proton acceptor and $\Delta\nu$ which serves as a measure of the strength of the hydrogen bond.[10b,12] For intramolecular hydrogen bonding, added complications due to steric effects must be considered.[13] For example, if the size of the proton acceptor (B) affects either the H–B distance or the angle formed by O–H–B, the value of $\Delta\nu$ will be affected even though the basicity of B is held constant.[13,14] We may now consider the validity of using intramolecular hydrogen bonding data derived from I and II where a 1,5 interaction occurs as a measure of the relative basicities of the ether and peroxide groups. Since the proton acceptor (B) is held constant as oxygen in I_B and II_B, no difficulties in varying the size of B will be encountered. In addition, the bond angles included in the five-membered ring in I_B and II_B should be approximately the same. Polar effects should be considered which could vary the acidity of the alcoholic hydrogen atom. These effects appear unimportant as seen from the constant values of ν_F in I, II, and III. It seems reasonable the somewhat smaller values of $\Delta\nu$ and $-\Delta H_{IB}$ for I compared with those for II (Table IV) are indicative of the peroxide group being less basic than the ether group.

A considerable amount of data has been rationalized with the aid of the Thorpe–Ingold hypothesis.[15] In particular, intramolecular hydrogen bonding of glycols may be explained, at least in part, using this hypothesis.[16] Our results for the hydroxy ethers, where there is a single proton donor in the molecule, can be interpreted with the aid of the Thorpe–Ingold effect. Before considering the effect of 2,2-dialkyl substitution in 2-alkoxy alcohols, it is well to consider the change in $\Delta\nu$ with varying alkyl substitution on the ether oxygen atom. The $\Delta\nu$ values for 2-methoxyethanol (IVa),[8c,17] 2-ethoxyethanol (IVb),[12b] and 2-*n*-butoxyethanol (IVc)[17] are 31–32, 30, and 31 cm^{-1}, respectively. Similar values of $\Delta\nu$ are reported for ethylene glycol.[15b,18] Increasing the bulk of the group bonded



IVa, R_1 = H; R_2 = CH_3
b, R_1 = H; R_2 = C_2H_5
c, R_1 = H; R_2 = *n*-C_4H_9
d, R_1 = CH_3; R_2 = H



Va, R_1 = H; R_2 = H
b, R_1 = H; R_2 = CH_3
c, R_1 = H; R_2 = C_2H_5
d, R_1 = CH_3; R_2 = H
III, R_1 = CH_3; R_2 = *t*-C_4H_9

to oxygen appears to have little or no effect on 1,5 intramolecular hydrogen bonding. Incorporation of a *gem*-dimethyl group into the glycol system to give 2-methyl-1,2-propanediol (IVd) results in a change in $\Delta\nu$ of 19 cm^{-1} ($\Delta\nu = 51$ cm^{-1}).[19] The increase in $\Delta\nu$ is attributed to an increase in the angle formed by CH_3–C_2–CH_3 and thus a decrease in the angle produced by C_3–C_2–O (*i.e.*, the Thorpe–Ingold effect). If a *gem*-dimethyl group is similarly introduced into the hydroxy ether system to give II, a corresponding change in $\Delta\nu$ of about 23 cm^{-1} (to $\Delta\nu = 54$ cm^{-1}) is observed. Again the Thorpe–Ingold effect may be conveniently employed to explain this change in $\Delta\nu$. The *gem*-dimethyl effect is then substantially the same in glycols and hydroxy ether for 1,5 intramolecular hydrogen bonding.

Although $\Delta\nu$ remains nearly constant for 1,5 hydrogen bonding when R_2 in IVa–c is varied, the value of $\Delta\nu$ for 1,6 hydrogen bonding changes when R_2 is varied in Va–c. The $\Delta\nu$ values for 1,3-propanediol (Va),[16] 3-methoxy-1-propanol (Vb),[17] and 3-ethoxy-1-propanol (Vc)[20] are 79.0, 87, and 90 cm^{-1}, respectively. When *gem*-dimethyl substitution is introduced into the 1,3-diol system to give Vd, the value of $\Delta\nu$ is 88

(11) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **71**, 2903 (1967), and references cited therein.

(12) (a) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co. San Francisco, Calif., 1960, p 90. (b) P. von R. Schleyer and R. West, *J. Amer. Chem. Soc.*, **81**, 3164 (1959); (c) S. Andreades and D. C. England, *ibid.*, **83**, 4670 (1961); (d) J. R. Gerslen, *J. Org. Chem.*, **26**, 758 (1961); (e) H. H. Freedman, *J. Amer. Chem. Soc.*, **83**, 2900 (1961).

(13) A. W. Baker and W. W. Kaeding, *ibid.*, **81**, 5904 (1959).

(14) Reference 2, p 122.

(15) (a) R. M. Beesley, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, **107**, 1080 (1915); (b) C. K. Ingold, *ibid.*, **119**, 305 (1921).

(16) P. von R. Schleyer, *J. Amer. Chem. Soc.*, **83**, 1368 (1961), and references cited therein.

(17) M. St. C. Flett, *Spectrochim. Acta.*, **10**, 21 (1957).

(18) (a) G. Chiurdoglu, R. deGroote, W. Masschelein, and H. van Risseghem, *Bull. Soc. Chim. Belges*, **70**, 342 (1961); (b) M. Kuhn, W. Lüttke and R. Mecke, *Z. Anal. Chem.*, **170**, 106 (1959).

(19) L. P. Kuhn, *J. Amer. Chem. Soc.*, **80**, 5950 (1958).

(20) F. T. Wall and W. F. Claussen, *ibid.*, **61**, 267 (1939).

cm^{-1}. Compared to 1,3-propanediol (Va), the *gem*-dimethyl substitution increases $\Delta\nu$ by 9 cm^{-1}. In contrast, the introduction of a *gem*-dimethyl group along with R_2 = *t*-butyl to give III results in a $\Delta\nu$ value of 128 cm^{-1}. This large change in $\Delta\nu$ for III as compared to the 1,3-propanediol systems must be due to a combination of the *gem*-dimethyl substitution as well as substitution on the ether oxygen atom.

Experimental Section[21]

2-*t*-Butylperoxy-2-methyl-1-propanol (I).—Isobutylene oxide[22] (180 g, 2.50 mol) was added slowly with efficient stirring to a solution of 90% *t*-butyl hydroperoxide (250 g, 2.50 mol, U. S. Peroxygen Corp.) and 0.5 ml of 30% sulfuric acid while the temperature was kept below 15°. The reaction mixture was stirred at room temperature for 2 days. The organic phase was separated and washed twice with 60 ml of water. Washings with sodium bicarbonate solution were continued until the organic phase was no longer acidic. After drying over magnesium sulfate, vacuum distillation through a 45 cm glass helices packed column gave 80 g (20% yield) of I, bp 38–40° (3 mm). The structure of I was established by its ir spectrum [O–H, 3638 (free) and 3593 (bonded); C–O, 1190 and 1143 ; O–O, tentative 865 cm^{-1}] and nmr spectrum (*gem*-dimethyl protons, 1.13 ppm, singlet, area = 6; *t*-butyl protons, 1.20, singlet, area = 9; CH_2 protons, 3.43, singlet, area = 2; OH proton, 2.35, area = 1).

Anal. Calcd for $C_8H_{18}O_3$: C, 59.23; H, 11.18. Found: C, 59.06; H, 11.29.

2-Methyl-2-neopentoxy-1-propanol (II).—Isobutylene oxide[22] (75.0 g, 1.04 mol) was added slowly with stirring to a mixture of neopentyl alcohol[23,24] (76.0 g, 0.864 mol), 0.3 ml of 50% sulfuric acid, and 16 g of carbon tetrachloride while the temperature was kept below 38°. Stirring was continued for an additional 12 hr at room temperature. The organic phase was separated, washed twice with 40 ml of water, and finally washed free of acid with sodium bicarbonate solution. After drying over magnesium sulfate, simple vacuum distillation gave 38 g (28% yield) of II, bp 38–39° (2 mm). The structure of II was confirmed by its infrared [O–H, 3638 (free), 3584 (bonded); C–O, 1145, 1075, 1045 cm^{-1}] and nmr (*t*-butyl protons, 0.85 ppm, singlet, area = 9; *gem*-dimethyl protons, 1.07, singlet, area = 6; OH proton, 2.42, area = 1; CH_2 protons, 2.93, singlet, area = 2 and 3.26, singlet, area = 2) spectra.

Anal. Calcd for $C_9H_{20}O_2$: C, 67.45; H, 12.57. Found: C, 67.52; H, 12.44.

3-*t*-Butoxy-2,2-dimethyl-1-propanol (III).[25]—A solution of 2,2-dimethyl-1,3-propanediol (100 g, 0.961 mol), *t*-butyl alcohol (81.0 g, 1.09 mol), and 200 ml of chloroform was added to 200 ml of 50% sulfuric acid with mechanial stirring while the reaction flask was cooled in an ice bath. The reaction mixture was stirred for an additional 48 hr at room temperature. The organic phase was separated and dried over magnesium sulfate, and the solvent was then removed by simple distillation. Vacuum distillation of the residue gave 30.0 g (19.5% yield) of III, bp 70–75° (8 mm). Redistillation gave a heart cut which showed only one peak by glpc analysis. The structure of III was established by its infrared [O–H, 3638 (free) and 3510 (bonded); C–O, 1070 and 1190 cm^{-1}], nmr (*gem*-dimethyl protons, 0.85 ppm, singlet, area = 6; *t*-butyl protons, 1.18 singlet, area = 9; CH_2 protons, 3.28, singlet, area = 2 and 3.15, singlet, area = 2; OH proton, 2.67, area = 1), and mass[26] (parent peak, *m/e* 160 (weak); $CH_2\overset{+}{=}OC(CH_3)$, 87; and $CH_2\overset{+}{=}OH$: 31) spectra.

Anal. Calcd for $C_9H_{20}O_2$: C, 67.45; H, 12.57. Found: C, 67.15; H, 12.51.

Infrared Spectra.—A Perkin-Elmer Model 621 grating spectrophotometer was employed. The temperature measurement and thermostating techniques were previously described.[5]

Registry No.—I, 17393-39-4; II, 17393-40-7; III, 17393-41-8.

Acknowledgments.—This investigation was supported by the U. S. Army Research Office (Durham, N. C.). Partial support for this work was also provided by the San Diego State Foundation through a Faculty Research Grant.

(21) All boiling points are uncorrected. Elemental microanalyses were performed by C. F. Geiger, Ontario, Calif. The nmr spectra were determined in 15% (w/v) carbon tetrachloride solutions on a Varian A-60 spectrometer with tetramethylsilane used as an internal standard. The mass spectra were measured with a Hitachi Perkin-Elmer RMU-6E spectrometer.

(22) H. O. House, *J. Amer. Chem. Soc.*, **77**, 5083 (1955).

(23) J. Hoffman, *Org. Syn.*, **40**, 76 (1960).

(24) We thank Mr. Gordon G. Snyder for the synthesis of this compound.

(25) We thank Mr. R. M. Castro for the preparation of this compound.

(26) See R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1967, Chapter 2.

Solvent Effects in the Decomposition of Benzoyloxy Radicals[1]

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Yields of CO_2 obtained in the decomposition of benzoyl peroxide in mixtures of hydrogen donor substrates and inert solvents have been used to determine the relative rates of hydrogen abstraction and decarboxylation of benzoyloxy radicals (k_a/k_d ratios). Kinetic schemes have been derived for both simple homolytic scission and induced decomposition and evaluated with cyclohexane and isopropyl alcohol, respectively. Measured k_a/k_d ratios show some variation with solvent, roughly paralleling the *t*-butoxy radical case. Relative rates of benzoyloxy radical attack on different substrates have been compared.

Although the course and rates of radical reactions usually show little solvent dependence, a few striking exceptions are known. The first to attract attention was the strong solvent dependence of the selectivity of chlorine atoms.[2] More recently we have shown that the competition between the hydrogen abstraction and β-scission reactions of *t*-butoxy and other alkoxy radicals is also solvent dependent, the medium having the greatest effect on the latter process.[3] Although complications arise in some systems,[4,5] our conclusions appear to remain quantitatively valid for hydrogen abstraction from aliphatic hydrocarbon substrates. Although aliphatic acyloxy radicals apparently undergo β-scission so rapidly that the process occurs largely within the solvent cage[6,7] benzoyloxy radicals from

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